

## MANUFACTURE OF SECONDARY BATTERY WITH GEL ELECTROLYTE

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### Abstract

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**PURPOSE:** To easily manufacture a thin, large-area secondary battery preventing the dropping of an active material and the deposition of dendrite, preventing the deterioration of the electrode active material at the time of production, and capable of obtaining the same surface impedance as that of an electrolyte solution.

**CONSTITUTION:** The manufacture of this secondary battery is provided with the first process in which a sheet or film-like polymer cross-linking body 1 is dipped in a solution 2 mixed with an electrolytic solution and a conductive polymer monomer to generate a gelatinous electrolyte 3 and the second process in which the gelatinous electrolyte 3 is sandwiched by two electrodes for assembling 4 and excitation 5 is applied.

# TRANSLATION FROM JAPANESE

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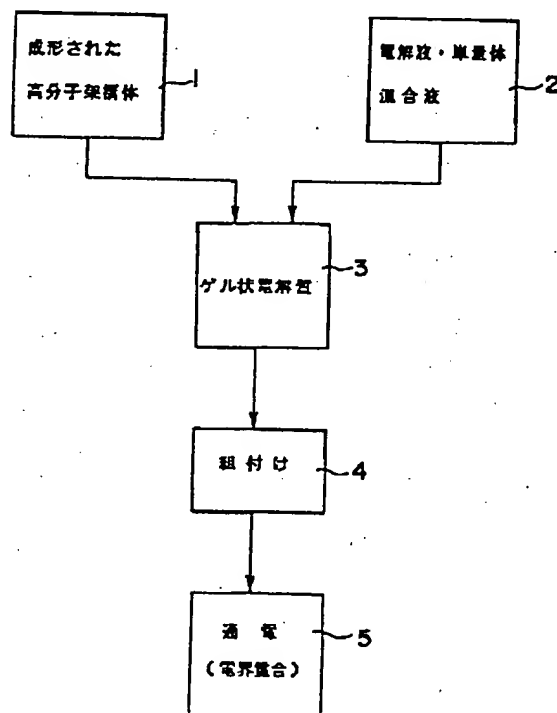
(54) [ Title of the Invention ] Method for Manufacturing Secondary Battery Using Gel Electrolyte

(57) [ Abstract ]

[ Object ] [To provide a method] with which a secondary battery that is thin and has a large surface area can be easily manufactured, dendrite precipitation and the fallout of the active material are prevented, the electrode active material undergoes no degradation during production, and interfacial impedance equivalent to that of an electrolytic solution can be obtained.

[ Constitution ] [The method] comprises a first step of producing a gel-form electrolyte 3 by dipping a crosslinked macromolecular sheet or film 1 in a solution 2 in which electrolyte is mixed with a conductive macromolecular monomer, and a second step of sandwiching this gel-form electrolyte 3 between two electrodes to produce a structure 4, and turning on the power (5).

- 1 molded and crosslinked macromolecular material
- 2 mixture of electrolyte and monomer
- 3 gel-form electrolyte
- 4 assembly
- 5 power on (electric field polymerization)



## [ Claims ]

[ Claim 1 ] A method for manufacturing a secondary battery using a gel electrolyte, characterized by comprising a first step of producing a gel-form electrolyte by dipping a crosslinked macromolecular sheet or film in a solution in which electrolyte is mixed with a conductive macromolecular monomer, and a second step of sandwiching this gel-form electrolyte between two electrodes and turning on the power, wherein the conductive macromolecule inside the gel or at the interface layer between the gel and the positive electrode is subjected to electric field polymerization, and at the same time the cations in the electrolyte are precipitated as the negative electrode active material at the interface layer between the gel and the negative electrode.

[ Claim 2 ] A method for manufacturing a secondary battery using a gel electrolyte as defined in Claim 1, characterized in that the conductive macromolecular monomer is paraphenylene, pyrrole, thiophene, aniline, or another organic compound having covalent bonds, or a derivative of one of these, and is one or more substances selected from the group consisting of substances that are able to undergo electric field polymerization in electrolyte, and have properties such that the anions in the electrolyte cause doping to proceed simultaneously with the electric field polymerization.

## Detailed Description of the Invention

[0001]

### Field of Industrial Utilization

The present invention relates to a method for manufacturing a secondary battery, characterized in that a gel is used for the electrolyte, and a conductive macromolecule is polymerized at the interfacial layer or in the interior of this gel to produce the electrode active material.

[0002]

### Prior Art

Among conventional secondary batteries, there are known types in which (A) a separator and an electrolytic solution or (B) a composite of polyethylene oxide and a sodium salt are/is interposed between positive and negative electrode sheets, for example.

[0003]

#### Problems Which the Invention is Intended to Solve

However, with a conventional secondary battery, and particularly one with the structure A above, it was difficult to pour in the electrolytic solution when producing a laminated battery that was thin and had a large surface area (eg, a unit cell thickness of about 1 mm and a surface area of at least  $30 \times 30$  cm). Another problem was that fallout of the active material and the precipitation of dendrite shortened the cycling life.

[0004] With the structure B above, because of the low conductivity of a solid electrolyte ( $10^{-4}$  S · cm or less), and because it was difficult to keep the electrodes in good contact with the solid electrolyte, interfacial impedance was high, which led to an increase in polarization.

[0005] Also, with a method for manufacturing a secondary battery of the above structure, after the electrode active materials were formed, they were assembled in a container and the electrolyte was poured in, and a problem encountered here was that the electrode active material was exposed to the air and degraded.

[0006] It is an object of the present invention to provide a method for manufacturing a secondary battery, with which (C) a secondary battery that is thin and has a large surface area can be produced easily, (D) fallout of the active material and precipitation of dendrite are prevented, which extends the cycling life, (E) the electrodes and the electrolyte are in better contact, resulting in an interfacial impedance that is the same as that of the electrolytic solution, and (F) a gel-form electrolyte containing a solution in which are mixed a monomer of a conductive macromolecule and liquid electrolyte is produced, and this gel-form electrolyte is sealed and then used as the electrode active material, so there is no contact with air that would cause the degradation of the electrode active material.

[0007]

#### Means Used to Solve the Above-Mentioned Problems

The method pertaining to the present invention for manufacturing a secondary battery using a gel electrolyte comprises a first step of producing a gel-form electrolyte by dipping a crosslinked macromolecular sheet or film in a solution in which electrolyte is mixed with a conductive macromolecular monomer, and a second step of sandwiching this gel-form electrolyte between two electrodes and turning on the power.

[0008] The result of these steps is that the conductive macromolecule inside the gel or at the interface layer between the gel and the positive electrode is subjected to electric field polymerization, and at the same time the cations in the electrolyte are precipitated as the negative electrode active material at the interface layer between the gel and the negative electrode.

[0009]

#### Operation of the Invention

With the present invention, it is easy to manufacture a secondary battery that is thin and has a large surface area, and furthermore the electrode active material undergoes no degradation while being produced.

[0010]

#### Examples

Fig. 1 is a block diagram illustrating an example of the method pertaining to the present invention for manufacturing a secondary battery using a gel electrolyte. In this figure, 1 is a first step in which a conductive macromolecule such as acrylic rubber is made into a sheet or film, for example, and 2 is a second step in which a pyrrole monomer is mixed with a 2.0 mol/L propylene carbonate solution of lithium perchlorate, for example, to produce an electrolyte/monomer mixture.

[0011] 3 is a third step in which the conductive macromolecule produced in the first step is dipped in the electrolyte/monomer mixture produced in the second step, and a gel-form electrolyte is produced through a swelling process.

[0012] 4 is a fourth step in which the gel-form electrolyte obtained in the third step is sandwiched between two platinum electrodes (not shown), and the outer periphery thereof is sealed with a thermoplastic resin film.

[0013] 5 is a fifth step in which a specific voltage, such as 4.0 V, is applied to the above-mentioned platinum electrodes (not shown) by a constant voltage power supply (not shown), a conductive macromolecule (polypyrrole) is subjected to electric field polymerization inside the gel or at the gel interface layer on the positive electrode side while the power is on, and at the same time the negative electrode active material (metallic lithium) is precipitated at the gel interface on the negative electrode side.

[0014] Next, the method for manufacturing a secondary battery using a gel electrolyte with the above structure will be described through reference to Figs. 2 and 3. For example, a conductive macromolecule such as acrylic rubber is made into a sheet or film (first step). Meanwhile, a pyrrole monomer is mixed with a 2.0 mol/L propylene carbonate solution of lithium perchlorate, for example, to produce an electrolyte/monomer mixture (second step).

[0015] Then, the conductive macromolecule produced in the first step is dipped in the electrolyte/monomer mixture produced in the second step, and a gel-form electrolyte 6 is produced through a swelling process. Then, as shown in Fig. 2, the gel-form electrolyte 6 thus obtained is sandwiched between two platinum electrodes 7a and 7b, and the outer periphery thereof is sealed with a thermoplastic resin film 8.

[0016] A specific voltage, such as 4.0 V, is then applied by a constant voltage power supply (not shown) to the platinum electrodes 7a and 7b, whereupon, as shown in Fig. 3, the conductive macromolecule (polypyrrole) 9 is subjected to electric field polymerization inside the gel or at the gel interface layer on the positive electrode side while the power is on, and at the same time the negative electrode active material (metallic lithium) is precipitated at the gel interface on the negative electrode side, so that the structure can function as a secondary battery.

[0017] The conductive macromolecule was acrylic rubber in the above description, but is not limited to this, and urethane, acrylonitrile butadiene rubber, hydrin rubber, fluororubber, polyether, polyester, polyimine, polyvinyl alcohol, polyacrylic acid, and other such highly polar organic compounds and crosslinked derivatives thereof can, of course, be used.

[0018]

Effect of the Invention

As described in detail above, the method of the present invention for manufacturing a secondary battery using a gel electrolyte provides many benefits, such as (a) a secondary battery that is thin and has a large surface area can be produced easily, (b) fallout of the active material and precipitation of dendrite are prevented, (c) there is no degradation of the electrode active material during production, which affords good stability of electrical capacity and cycling characteristics during charging and discharging, and (e) [sic] interfacial impedance that is the same as that of the electrolytic solution is obtained.

#### Brief Description of the Figures

Fig. 1 is a block diagram illustrating an example of the method pertaining to the present invention for manufacturing a secondary battery using a gel electrolyte;

Fig. 2 is a diagram illustrating the manufacturing method in Fig. 1; and

Fig. 3 is a diagram of the function [of the product] as a secondary battery obtained with the manufacturing method illustrated in Fig. 1.

#### Key:

- 1 first step
- 2 second step
- 3 third step
- 4 fourth step
- 5 fifth step
- 6 gel-form electrolyte
- 7a and 7b platinum electrodes
- 8 thermoplastic resin film
- 9 conductive macromolecule
- 10 negative electrode active material

Figure 1

- 1 molded and crosslinked macromolecular material
- 2 mixture of electrolyte and monomer
- 3 gel-form electrolyte
- 4 assembly
- 5 power on (electric field polymerization)

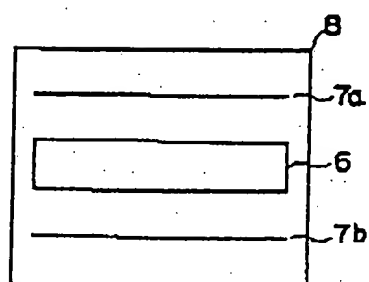
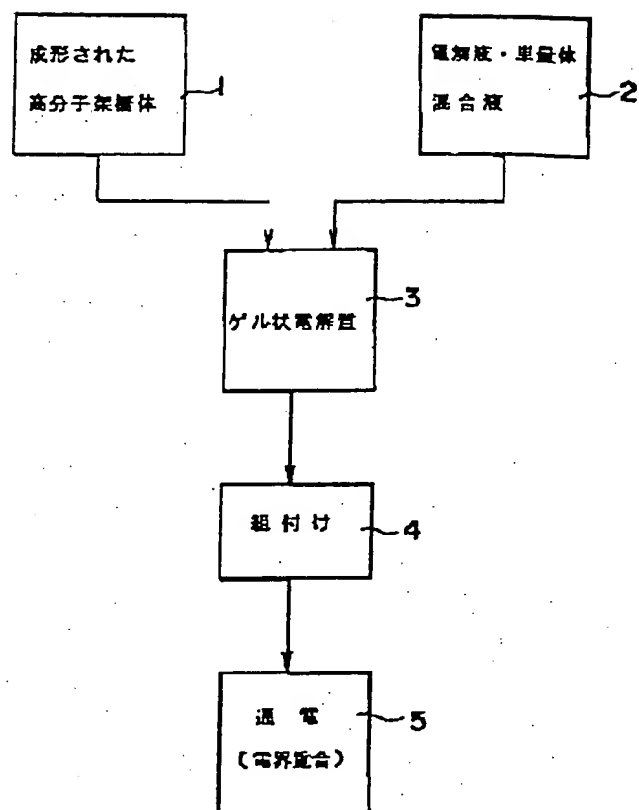


Figure 2

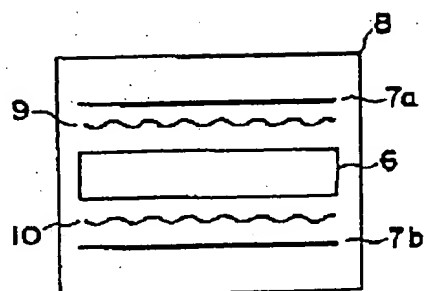


Figure 3